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REVIEW

Kinetic analysis of cellulose pyrolysis: a short review

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Since the 1950s, cellulose pyrolysis has been the subject of intense study, with kinetic analyses forming a major part of these studies. They represent useful tools for a better understanding of the physicochemical process and for the proper design of industrial pyrolysis units. Until recently, the methods most frequently used in these analyses were based on model-fitting, i.e. the fitting of the experimental data to a number of mathematical models. Nowadays, other methods, so-called "model-free" methods, are considered to be more suited. These are based on the principle that, at constant conversion, the reaction rate depends only on temperature. In its first part, this short review presents the particularities and drawbacks of the traditional model-fitting models. Subsequently, several main contributions in this field are listed and discussed. Finally, the more suited "model-free" (isoconversional) methods are explained and several main studies presented, as well as a comparison of this method with the model-fitting ones.
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Keywords: cellulose pyrolysis, model-fitting kinetic methods, isoconversional methods, TGA.

Introduction

Cellulose is the most abundant biopolymer on earth. It is found in the stalks of vegetal species and in wood. Cellulose is usually isolated from wood by an acidic treatment, affording a wood pulp, of which the insoluble fraction is denoted as "α-cellulose". It is the type of cellulose in most frequent use in the pharmaceutical and food industries. A high content of this compound is found in the white cotton fibres (around 94–96 mass %) which are considered to be pure cellulose. Cotton cellulose is used for manufacturing microcrystalline cellulose (MCC) and filter paper.

Together with hemicellulose and lignin, cellulose is an important compound of biomass, representing from 50 mass % up to 75 mass %. This is one of the reasons behind the intensive studies of cellulose as a case model for wood and biomass pyrolysis. Nowadays, pyrolysis is a promising environmentally-friendly technical process for reduction of greenhouse gases emissions and valorisation of wastes. The amount of CO_2 released during biomass pyrolysis is equal to that absorbed by the plant during its growth. Despite these advantages, in 2008 there were only 30 to 50 high capacity commercial pyrolysis plants in existence worldwide. This stemmed from the drawbacks represented in particular by the endothermic character of the process and the necessity of treating the solid and liquid fractions obtained for a more adequate valorisation.

An extensive literature exists on cellulose pyrolysis, as pyrolysis represents a promising way of obtaining fuels from renewable sources. Thus, in 2010, in Germany, energy consumption from biomass represented 7.9 %, out of a total of 11 % of renewable energy (AGEE-Stat, 2011). However, little progress has been made up to the present and the real mechanism has not yet been found.

This review summarises the main contributions on the subject of cellulose pyrolysis kinetics published in the open literature. Two directions are emphasised: the model-fitting vs the so-called "model-free" methods. First, the drawbacks of the classical model-fitting techniques are outlined. Next, the main reasons for regarding the "model-free" methods as more suitable are considered. A comparative discussion of the two methods is also presented. However, it should be noted that this short review covers partially only the existent literature on the kinetic analysis of cellulose pyrolysis at different heating rates (from slow to flash).

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Problems regarding thermo-analytical kinetic modelling of solids decomposition

At the beginning of the 21st century, Galwey (2004) emphasised the major problem with kinetic studies based on thermal analysis experiments. Among his conclusions, the lack of physical meaning for the Arrhenius parameters calculated and the impossibility of finding a real kinetic mechanism for the process from thermal analysis data alone are worth noting. According to the same author, supplementary tests (X-ray analysis, microscopy, etc.) are required. In the thermo-analytical literature at that time he also identifiedthe existence of ambiguities in the definition of essential terms (“mechanism”, “rate constant”, “activation energy”) and a lack of order in the results presented. Little progress has yet been made in resolving these problems.

Accordingly, the main drawback of this kind of approach, dealing with the Arrhenius parameters calculated, remains unsolved. As Vyazovkin and Wight (1997) stated, “if we are to interpret them in terms of the transition-state theory, they are not applicable to solid state reactions”. In the solid state reactions, due to the stable and tight array-structure of the sample, the energy distributions functions of Maxwell–Boltzmann are not suited. However, other energy distribution functions can be used such as the Fermi–Dirac function for electrons and the Bose–Einstein function for photons. In this case, E_a is related to the activation enthalpy and A is related to the frequency of lattice vibrations, as also stated by Vyazovkin and Wight (1997). The physical significance of these parameters refers to the elemental processes of solids, i.e. nucleation, nuclei growth, etc. Meanwhile, from thermo-analytical experiments, the general kinetic parameters are obtained. Another major problem of this kind of approach is the empirical nature of the kinetic models tested (White et al., 2011). Further investigations are needed in order to identify the real mechanism of solids’ degradation, due to the fact that,in this case, the thermal changes (including the chemical changes) are often more complex than is recognised.

All these problems represent a consequence of the origins of modern thermal analysis kinetics, as noted by Galwey (2004). These origins are located in a specialised branch of chemistry concerned with the thermal decomposition of solids, known as “crystolysis reactions”. The theory applied in these cases was based on geometric models applicable to heterogeneous reactions in crystals. For these crystals, the stoichiometries were regarded as already well established.

In conclusion, for solid state thermal degradation kinetics, studied using the thermal analysis methods, the values of the Arrhenius parameters calculated describe a given step of the process in a general manner and have a different physical meaning than in the case of gas or liquid phase transformations.

Main contributions to cellulose pyrolysis model-fitting kinetic models

Several models describing the cellulose pyrolysis kinetics have been published with different degrees of accuracy. As Di Blasi (1993) stated, the studies of cellulose pyrolysis largely followed the chemical regime conditions (intrinsic kinetics) while several attempted to model the process under ablative regime conditions (apparent kinetics). Ablative pyrolysis is contact pyrolysis, allowing large particles to be treated as in flash pyrolysis (Lédé, 2012). The intrinsic kinetics conditions provide the information for identifying the real degradation mechanism of cellulose pyrolysis. Despite huge efforts, the real kinetic model remains unknown. From the perspective of the chemical transformations, this process is regarded as proceeding in three stages, differentiated by the temperature range (Garcia-Perez, 2008). Thus, the pyrolysis stage is the first thermal degradation observed at temperatures up to 700 ℃. The second stage between 700–850 ℃ is represented by the secondary pyrolysis. Finally, tertiary reactions generally occur between 850–1000 ℃. Globally, the pyrolysis reaction comprises homogeneous solid-phase processes, heterogeneous solid–vapour interactions, and also gas-phase transformations.

Garcia-Perez (2008) proposed a detailed complex model for cellulose and biomass pyrolysis, explaining the formation of some secondary pyrolysis products (PAHs). Furthermore, he identified the main products and their formation mechanisms from each stage. Thus, in the primary pyrolysis stage, cellulose-derived molecules are formed as fluid species, namely levoglucosane (LVG) and hydroxylacetaldehyde. From the secondary pyrolysis stage, gaseous olefins, aromatics, CO, CO_2, H_2O, H_2, and secondary condensed oils (phenols, aromatics) are produced. Finally, from the tertiary reactions stage, PAHs are formed together with non-condensable gases (CO, CO_2, H_2, H_2O). The PAHs formed in the course of cellulose pyrolysis are either gases, such as the methyl derivatives of aromatics (toluene, indene, methyl acenaphthylene, methyl naphthalene)or condensed gases or tars, like naphthalene, acenaphtylene, anthracene/phenantrene, and pyrene. Coke and soot are formed in the primary and secondary reactions. Evans and Milne (1987) noted that coke (“char”) was formed by liquid and organic vapours thermolysis, while soot was formed by the homogeneous nucleation of high temperature decomposition products of hydrocarbons in the gas phase processes. It is generally accepted that a degradation step takes place prior to pyrolysis. Kilzer and Broido (1965) were the first to observe this. They explained the evolution of water during this stage as being the effect of exothermic cross-linking reactions. The corresponding temperature range is approximately 100–220 °C, as confirmed in a recent study by Zhu et al. (2012) who used an in-situ visualisation technique. The same study confirmed that the primary pyrolysis step occurred in the temperature range of 230–380 °C for a final experimental temperature of 500 °C.

On the basis of the above chemical mechanisms for cellulose pyrolysis, the existing global kinetic models for this process were developed. A classification of the kinetic models for pyrolysis is given by Di Blasi (1993) as follows: (a) one-step global reaction with no prediction of product yields dependence on reaction conditions; (b) multi-reaction empirical models correlating experimental data with several reactions; (c) semi-global models which include primary and secondary reactions with lumped pyrolysis products (tar, gas, and "char"). As noted by Lédé (2012), the most representative models for cellulose pyrolysis were published between 1950 and 1980. The same author states that these models are classified into two main categories: models that take into account the formation of an intermediate and models that neglect its formation.

Fig. 1 presents an historical overview (Capart et al., 2004; White et al., 2011; Lédé, 2012) of the most important model-fitting kinetic models of the cellulose pyrolysis. In this figure, the abbreviations of the listed models are given in the grey boxes. The following notations were used for the different types of reactions considered in the kinetic models listed, namely by their corresponding kinetic constants (see Fig. 1):

$$\text{Cellulose} \xrightarrow{k_1} \text{Char} \tag{1}$$

$$\text{Cellulose} \xrightarrow{k_2} \text{Tar} \tag{2}$$

$$\text{Cellulose} \xrightarrow{k_3} \text{Gases} \tag{3}$$

$$\text{Cellulose} \xrightarrow{k_4} \text{Intermediate} \tag{4}$$

$$\text{Low DP cellulose} \xrightarrow{k_5} \text{Activecellulose (AC)} \tag{5}$$

$$\text{Cellulose} \xrightarrow{k_6} \text{Char} + \text{Tar} \tag{6}$$

$$\text{Cellulose} \xrightarrow{k_7} \text{Char} + \text{Gases} \tag{7}$$

$$\text{Cellulose} \xrightarrow{k_8} \text{Char} + \text{Tar} + \text{Gases} \tag{8}$$

$$\text{Intermediate} \xrightarrow{k_9} \text{Char} \tag{9}$$

$$\text{Intermediate} \xrightarrow{k_{10}} \text{Tar} \tag{10}$$

$$\text{Intermediate} \xrightarrow{k_{11}} \text{Gases} \tag{11}$$

$$\text{Intermediate} \xrightarrow{k_{12}} \text{Char} + \text{Gases} \tag{12}$$

$$\text{Tar} \xrightarrow{k_{13}} \text{Gases} \tag{13}$$

$$\begin{gathered} \text{Tar} \xrightarrow{k_{14}} \text{Char} + \text{Gases} \\ \text{Intermediate} \xrightarrow{k_{14}} \text{Char} + \text{Gases (BRmodel)} \end{gathered} \tag{14}$$

$$\text{Tar} \xrightarrow{k_{15}} \text{Char} + \text{Gases} \tag{15}$$

$$\text{Tar} \xrightarrow{k_{16}} \text{Char} \tag{16}$$

$$\text{Char}_1 \xrightarrow{k_{17}} \text{Char}_2 + \text{Gases} \tag{17}$$

$$\text{Char}_2 \xrightarrow{k_{18}} \text{Char}_3 + \text{Gases} \tag{18}$$

A classification of all the models reviewed is given below. This considers the linkage or otherwise of the final lumped products obtained (names of the models underlined are those taking into consideration the formation of an intermediate, usually AC):

i) Tars, gases, chars:

– Model 3R (Agrawal, 1988) with three parallel reactions directly from cellulose;

– Model MKB (Agrawal (1988), "modified Kilzer–Broido" model);

– Model L (Lewellen et al., 1977) is a complex kinetic model which explains the decomposition steps both in the cellulose matrix and in the ambient atmosphere of the sample; the intermediate is LVG;

– Model GP (Garcia-Perez, 2008) based on a literature review regarding the formation of PAHs from biomass pyrolysis.

ii) Char + tar + gases:

– Model F1 (Stamm, 1956) is the first kinetic model for cellulose pyrolysis; it is the 1st order kinetic model formulated for the pyrolysis data from Douglas fir cellulose;

– Model V1 (Várhegyi et al., 1997) for high-pressure conditions and sealed crucibles proving that water catalyses the process.

iii) Char + tar + gases, gases:

– Model BSZ (Banyasz et al., 2001).

iv) Char + gases, tar, gases:

– Models S1 (Shafizadeh, 1968) and S2 (Shafizadeh, 1982) with the difference that S1 takes into account the transformations of gases into "char + gases" and the inverse;

– Model DKM (Diebold, 1994) considers the secondary pyrolysis that consists of the degradation of tars to gases at high temperatures;

– Model W (Scott et al., 1989), "Waterloo" pyrolysis, based on flash pyrolysis experiments on Avicel cellulose in a fluidised bed reactor operating at 520 °C and 101 kPa.

v) Char + gases, tar:

– Model B (Broido & Nelson, 1975) is the first semi-global model; it assumes the formation of an intermediate denoted as AC ("active" cellulose or "anhydrocellulose") and the further degradation of the primary "char + gases" into secondary and subsequently tertiary "char + gases";

– Model KB1 (Kilzer & Broido, 1965);

– Model BS (Shafizadeh & Bradbury, 1979),"Broido–Shafizadeh" model, is frequently cited in the literature for cellulose pyrolysis; it was established from pyrolysis experiments under vacuum (2 kPa); this was needed to prevent secondary reactions and to improve recovery of the primary products;

– Model V2 (Várhegyi et al., 1997) considers AC to contain a mixture of cellobiose, cellotriose, other polymers of cellobiose, glucose, and fructose;

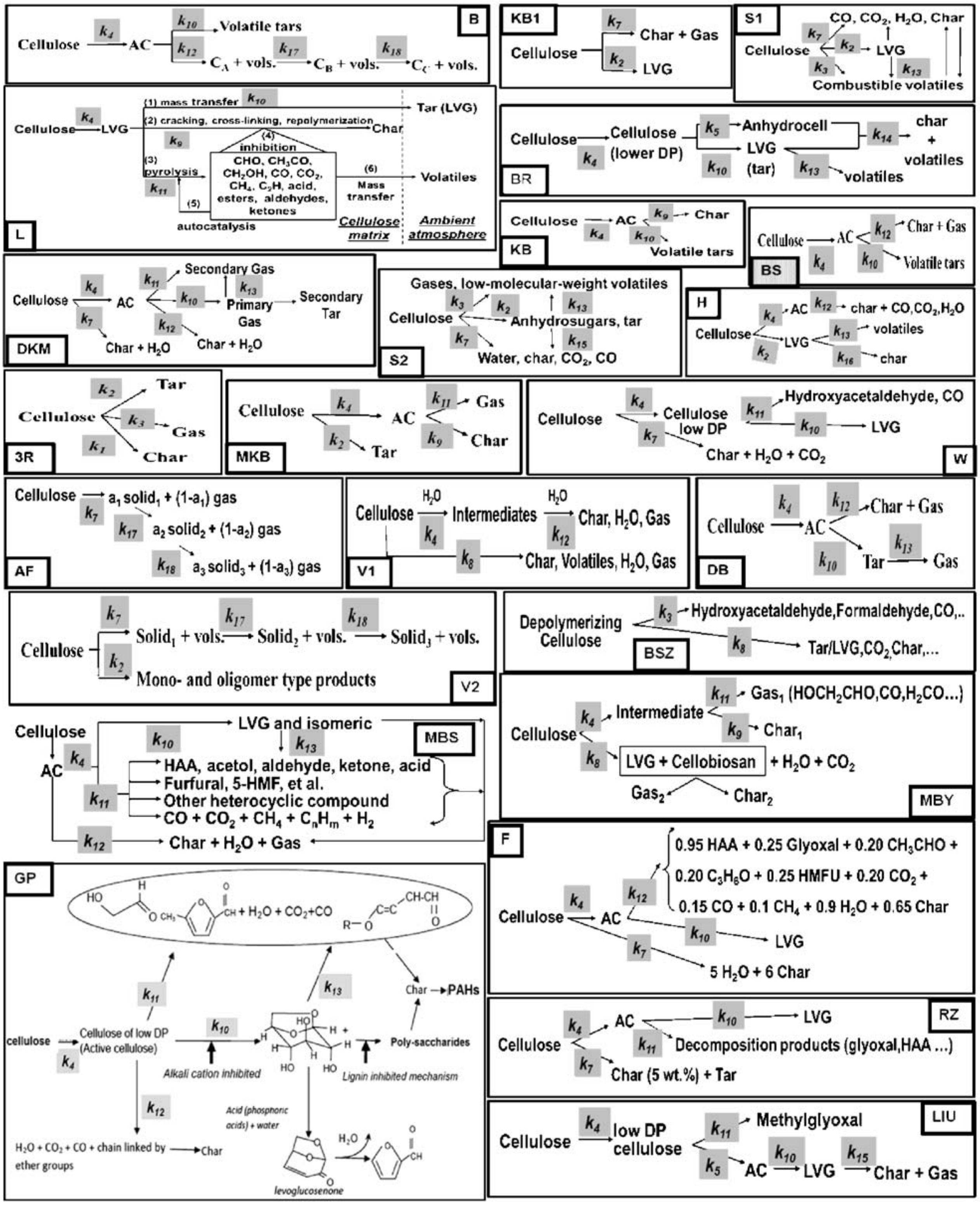

Fig. 1. Most important semi-global model-fitting kinetic models for cellulose pyrolysis published (AC = active cellulose/cellulose intermediate, HMFU/5-HMF = 5-hydroxymethyl furfural).

– Model LIU (Liu et al., 2008);

– Model F (Ranzi et al., 2008) is a detailed kinetic model, taking many elementary reactions into account.

vi) Char + gases, gases:

– Model BR (Broido et al., 1973) takes into account the formation of lower DP cellulose, AC, and LVG as intermediates;

– Model DB (Di Blasi, 1996) introducing a supplementary reaction which takes the secondary pyrolysis into account, i.e. the degradation of tars into gases at high temperatures.

vii) Char + gases:

– Model AF (Alves & Figueiredo, 1989) considers further degradation of the primary "char + gases" into secondary and subsequently tertiary "char + gases";

– Model MBS (Liao et al., 2004) also considers the secondary reactions of levoglucosan and gases cracking.

viii) Char + tar, tar, gases:

– Model RZ (Ranzi et al., 2008) is a multi-step lumped mechanism based on TGA experiments previously published.

ix) Char + gases, char, gases:

– Model H (Hopkins et al., 1984) is based on flash pyrolysis experiments.

x) Char, tars:

– Model KB (Broido, 1976) is based on experiments realised from TGA under vacuum.

xi) Char, gases:

– Model MBY (Mamleev et al., 2007) considers the intermediate formation of cellobiosan linked with LVG and gases.

All these models neglect the mass and heat transfer phenomena that become rate-limiting when a high mass of the sample and/or high temperatures are used. In this case, other models are needed, at intra-particle level; this case is not discussed below. Of the models listed above, the first order global model (F1) was intensively used for this process in the literature. Moreover, out of the semi-global models, the BS model is the most important, and is still considered as a reference for the kinetic modelling of cellulose pyrolysis, albeit contested by Várhegyi et al. (1994). New models were proposed in the last decade and are considered better than the BS model or its derivatives, all of which have as their main drawback the fact that they take into account the formation of an intermediate. This was and remains a controversial issue in cellulose pyrolysis, since any such intermediate is difficult to identify and quantify.

The new models consider that a kinetic of nuclei-growth best describes the process. The models used for describing this phenomenon are either of the Avrami–Erofeev or of the Prout–Tompkins type (Capart et al., 2004; Mamleev et al., 2009; Barud et al., 2011). It is important to note that these nuclei-growth models give similar results to the "model-free" methods. In this concept, Mamleev et al. (2009) proposed a mechanism involving the formation of several melted cavities (nuclei) with an encapsulated liquid inside the cellulose's microfibre. More recently, Sánchez-Jiménez et al. (2011) proposed a new model which was better than the Avrami–Erofeev, Prout–Tompkins, or other nucleation or growth mechanisms. This new model is an acceleratory chain-scission model based on breakage of the polymeric cellulosic chains. In addition, it makes no assumptions as to the exact chemical nature of the bond breakages. Another type of model applied to the kinetic study of this process was a statistical model, known as "the distributed activation energy model" (DAEM) (Sonobe & Worasuwannarak, 2008). This has been in use for biomass kinetic analysis since 1985 but it has attracted little interest among the scientists from this domain.

The first order (F1) model is considered by Banyasz et al. (2001) as satisfactorily describing the process at constant heating rates up to 100 ℃ min^{-1}. This is due to the negligible effect of the high temperatures pathway under these conditions. Moreover, Di Blasi stated that the F1 model could be considered as rigorously representative of intrinsic kinetics (Di Blasi, 1998). However, Völker and Rieckmann (2002) observed that the pyrolysis behaviour of small cellulose samples can be described more accurately by multi-step rather than by single-step processes.

Table 1 shows the published values for these parameters as calculated using the F1 model. Those references where the values of kinetic parameters varied with the heating rate are omitted from the list, since they may be regarded as unreliable on the basis of the ICTAC 2000 project conclusions that the use of isoconversional methods and multiple heating rates experiments are valuable tools for describing the multi-step thermo-analytical processes (Dickinson & Heal, 2009a, 2009b). However, studies of the F1 kinetic model performed with this type of cellulose are few. It can be seen that the use of microcrystalline cellulose (MCC) afforded values of these parameters which are among the highest (150–240 kJ mol^{-1} and 2.5×10^{17}–5.01×10^{21} min^{-1}). These are superior to those obtained using α-cellulose (including filter paper) or other types of cellulose. When using a nitrogen flow of 60–70 mL min^{-1} or a helium flow of 100–150 mL min^{-1}, it can be observed that the kinetic parameters' values increase with the decrease in the final reaction temperature, irrespective of heating rate, type of cellulose or sample mass. Thus, in the case of N_2 flow, at temperatures up to 1000 ℃, the corresponding kinetic parameters' values were: 2.82×10^{14} min^{-1} and 182.7 kJ mol^{-1}, while at 500 ℃ the values were higher: 3.01×10^{17} min^{-1} and 210 kJ mol^{-1}. For the He flow, at 1000 ℃ these values were: 6×10^{17} min^{-1} and 210 kJ mol^{-1}, while at 900 ℃ they were higher: 2.88×10^{18} min^{-1} and 226.5 kJ mol^{-1}. From the studies reviewed using the F1 kinetic model presented in Table 1, it can be seen that the calculated energy is situated in the range of 82.7–244 kJ mol^{-1} with a median of 192.3 kJ mol^{-1} and the pre-exponential factor range is 6.7×10^5–1.28×10^{20} min^{-1} with a median of 5.11×10^{19} min^{-1}.

Table 1. Published values for kinetic parameters of the first order model (F1) method for cellulose pyrolysis in inert atmosphere

Reference	Author/s, year (model)	A	E_a	Cellulose type or source	Equipment	Heating rate	Temperature range	Carrier gas	Carrier gas flow	Sample mass
		min^{-1}	kJ mol^{-1}			℃ min^{-1}	℃		mL min^{-1}	mg
Lédé (2012)	Stamm, 1956 (F1)	6.70×10^5	110.0	Douglas fir α-Cellulose	Oven	–	110–220	–	–	–
Font and García (1995)	Akita and Kase, 1967	9.96×10^{17}	223.6	α-Cellulose	TGA-DTA	Dynamic	–	–	–	–
Conesa et al. (1995)	Chatterjee and Conrad, 1966	3.30×10^{20}	175.7	Cotton (α-Cellulose)	–	–	–	–	–	–
Conesa et al. (1995)	Lipska and Parker, 1969	–	209.2	α-Cellulose (0.075 cm thick)	–	–	–	–	–	–
Conesa et al. (1995)	Lewellen and coworkers, 1977	4.07×10^{11}	139.0	Filter paper	–	–	–	–	–	–
Font and García (1995)	Antal and coworkers, 1980	4.20×10^{11}	153.0	–	TGA	Dynamic	–	–	–	–
Conesa et al. (1995)	Hajaligol and coworkers, 1982	1.20×10^{10}	132.8	Filter paper (0.0101 cm thick)	Screen heater	–	–	–	–	–
Font and García (1995)	Bilbao and coworkers, 1987	3.00×10^{19}	227.0	–	TGA	Dynamic	–	–	–	–
Font and García (1995)	Agrawal, 1988	9.18×10^{15}	204.8	Filter paper – Whatman	TGA	–	–	–	–	–
Font and García (1995)	Alves and Figueiredo, 1989 (AF)	6.78×10^{12}	167.2	Filter paper – Whatman	TGA	–	–	–	–	–
Várhegyi et al. (1989)	Várhegyi and coworkers, 1989	2.39×10^{19}	234.0	MCC – Avicel	TGS2^a	10	–	–	–	1–2
Font and García (1995)	Cordero and coworkers, 1990	2.82×10^{14}	182.7	α-Cellulose-Aldrich	TGA^b	5	RT-1000	N_2	70	15
Font and García (1995)	Várhegyi and coworkers, 1994	–	238.0	MCC – Avicel	TGA	2	RT-370	–	–	0.5–3
Conesa et al. (1995)	Conesa and coworkers, 1995	3.01×10^{17}	217.2	Filter paper – Whatman 6	TGA7^a	5, 10, 25, 50	RT-500	N_2	60	$\sim$ 3–4
Várhegyi et al. (1997)	Várhegyi and coworkers, 1997 (V2)	3.20×10^{18}	240.0	MCC – Avicel PH-105 Filter paper – Whatman1&42	TGS2^a	2, 5, 10, 20, 50, 80	250-370	Ar/He	140	0.3–3
Várhegyiet al. (1997)	Rao and Sharma, 1998	2.81×10^7	82.7	Cellulose	–	20	553-623	–	–	–
Grønli et al. (1999)	Grønli and coworkers, 1999	6.00×10^{20}	244.0	MCC – Avicel PH-105	SDT2960^c, TGA7^a, TGS2^a SDTA851^d STA409C^e	5–40	–	N_2	30–500	≤ 5
Huang et al. (2011)	Orfao and coworkers, 1999	6.84×10^{16}	210.0	–	–	5	–	–	–	–
Fisher et al.(2002)	Fisher and coworkers, 2002	6.00×10^{17}	210.0	MCC – Avicel PH-102	TGA^e	1–60	RT-700 (1000)	He	150	2–15
Huang et al. (2011)	Vamvuka and coworkers, 2003	1.28×10^{20}	231.8	Straw	TGA	10	–	N_2	–	–
Huang et al. (2011)	Yang and coworkers, 2004	3.36×10^{18}	227.0	–	–	10	–	–	–	–
Blažek (2005)	Blažek, 2005	2.77×10^{16}	164.4	MCC – Merck	TGA 92-16^f	10–30	–	N_2	27	20–40
Hu et al. (2007)	Hu and coworkers, 2007	–	233.0	α-Cellulose – Fluka	EXSTAR6000^g	2.5, 5, 10	300–900	N_2	200	3–7
Huang et al. (2011)	Huang and coworkers, 2011	2.88×10^{18}	226.5	Filter paper – Advantec	STA409CD^e	5	RT-900	He	100	10
Chen and Kuo (2011)	Chen and Kuo, 2011	2.86×10^9	124.4	α-Cellulose – Alfa Aesar	TGA Diamond^a	isothermal	200–300	N_2	200	$\sim$ 5

a) Perkin–Elmer; *b*) Thermoflex Rigaku; *c*) TA Instruments; *d*) Mettler Toledo; *e*) Netzsch; *f*) Setaram; *g*) Seiko Instruments Japan; MCC = microcrystalline cellulose, RT = ambient temperature.

Table 2. Published values for kinetic parameters of several main semi-global models of cellulose pyrolysis in inert atmosphere

Reference	Model	Year	A	E_{a}	Reaction constants	Reaction	Observations
			min^{-1}	kJ mol^{-1}			
Conesa et al. (1995)	KB1	1975	7.9×10^{11}	153.1	k_2	Eq. (2)	35 % char 65 % gas
			1.9×10^{16}	197.9	k_7	Eq. (7)	
		1995	2.3×10^{17}	217.7			
			3.2×10^{17}	225.5			
Di Blasi (1998)	BR	1998	4.7×10^{11}	152.8	k_4	Eq. (4)	Cellulose discs, 0.076 cm thick
			6.6×10^{16}	206.8	k_{10}	Eq. (10)	
			2.2×10^{17}	210.4	k_{14}	Eq. (14)	
		1979	1.7×10^{21}	242.4	k_4	Eq. (4)	Cellulose powder, 0.5 cm thick; isothermal tube furnace
			1.9×10^{16}	197.9	k_{10}	Eq. (10)	
			7.9×10^{11}	153.1	k_{12}	Eq. (12)	
Conesa et al. (1995)	BS	1995	1.1×10^{24}	274.4			Filter paper
			6.2×10^{10}	200.9			
			4.9×10^{16}	207.5			
Reed and Cowdery (1987)	DKM	1987	1.7×10^{21}	243.0	k_4	Eq. (4)	–
			4.0×10^{7}	109.0	k_7	Eq. (7)	
			2.1×10^{13}	204.0	k_{11}	Eq. (11)	
			1.1×10^{5}	61.0	k_{10}	Eq. (10)	
			7.8×10^{11}	153.0	k_{12}	Eq. (12)	
Conesa et al. (1995)	3R	1988	3.0×10^{13}	178.9	k_1	Eq. (1)	α-Cellulose
			2.0×10^{16}	200.6	k_8	Eq. (8)	
		1995	1.5×10^{17}	226.9			
			3.7×10^{17}	219.2			
Conesa et al. (1995)	MKB	1988	6.4×10^{15}	195.8	k_2	Eq. (2)	α-Cellulose
			1.8×10^{12}	159.3	k_4	Eq. (4)	
			3.4×10^{17}	214.6	k_{11}	Eq. (11)	
			1.9×10^{16}	203.7	k_9	Eq. (9)	
		1995	2.5×10^{8}	120.1			
			1.6×10^{24}	279.3			
			5.4×10^{16}	208.5			
			3.8×10^{15}	206.8			
Conesa et al. (1995)	AF	1989	7.3×10^{13}	174.0	k_7	Eq. (7)	Filter paper, $a_1 = 0.75$
			1.9×10^{14}	178.0	k_{17}	Eq. (17)	Filter paper, $a_2 = 0.99$
			1.2×10^{14}	179.0	k_{18}	Eq. (18)	Filter paper, $a_3 = 0.22$
		1989	1.3×10^{11}	139.0			Cotton wool, $a_1 = 0.87$
			4.2×10^{12}	157.0			Cotton wool, $a_2 = 1.00$
			1.1×10^{17}	209.0			Cotton wool, $a_3 = 0.16$
		1995	3.3×10^{17}	217.5			Filter paper, $a_1 = 0.70$
			6.7×10^{11}	128.2			Filter paper, $a_2 = 0.78$
			9.7×10^{12}	147.5			Filter paper, $a_3 = 0.16$
Miller and Bellan (1997)	DB	1994	1.7×10^{21}	242.4	k_4	Eq. (4)	–
			2.0×10^{16}	196.5	k_{10}	Eq. (10)	
			7.8×10^{11}	150.5	k_{12}	Eq. (12)	
			2.6×10^{8}	108.0	k_{13}	Eq. (13)	
Marra (2009)	KB	1997	1.3×10^{16}	167.5	k_4	Eq. (4)	$n_1 = 0$
			1.9×10^{15}	196.0	k_9	Eq. (9)	$n_2 = 1.5$
			5.6×10^{17}	216.6	k_{10}	Eq. (10)	$n_3 = 1.5$
Banyasz et al. (2001)	BSZ	2001	1.0×10^{16}	198.9	k_3	Eq. (3)	Filterpaper – Whatman 41
			1.4×10^{12}	148.2	k_8	Eq. (8)	
Ranzi et al. (2008)	F	2008	4.8×10^{15}	192.6	k_4	Eq. (4)	–

Table 2 shows the published values for the kinetic parameters calculated with several main global multi-step models (KB1, BR, BS, DKM, 3R, MKB, AF, DB, KB, BSZ, F). A wide scatter of parameter values can be observed, confirming the empirical character of the approaches used in these kinetic modelling studies. Because of this variation, no realistic assumptions can be made regarding the validity of the kinetic models tested. The variation is observed even for the same model when tested in different years by the same author, under the same experimental conditions (KB1, BR, 3R, MKB, AF).

Despite the large number of kinetic studies on cellulose pyrolysis, few insights into understanding of the process have been achieved. In general, the process chemistry is only globally described by pseudo-components which consider groups of chemical species. In conclusion, these models are important, especially for small samples where only intrinsic kinetics occurs. In the mid-nineties, Vyazovkin (1996) suggested the use of the term "kinetic scheme" instead of "mechanism" in the thermal analysis kinetic studies, as being more appropriate. These schemes represent a sequence of steps affecting or producing a modification of a measured physical property. The present author endorses this recommendation as suited for further studies in this field.

Main contributions to cellulose pyrolysis "model-free" kinetic models

Since Galwey's observations (Galwey, 2004) on the empirical nature of the kinetic parameters calculated by model-fitting methods, more authors have become aware of this problem. Thus, the so-called "model-free" methods were proposed as a solution. In the last decade these new methods have been used more and more frequently for the kinetic analysis of solids' thermal processes. They are based on the principle that, at constant conversion, the reaction rate depends only on temperature, as can be seen in the mathematical expression used for their description (Vyazovkin & Wight, 1997):

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}T^{-1}}\right]_\alpha = -\frac{E_\mathrm{a}}{R} \tag{19}$$

where α is the conversion, t/min is the time, T/K is the temperature, $E_\mathrm{a}/(\mathrm{kJ\ mol^{-1}})$ is the activation energy, and $R/(\mathrm{J\ mol^{-1}\ K^{-1}})$ is the universal gas constant.

For this reason they are also known as "isoconversional" methods. Usually, the E_a–α curves enable recognition of a multi-step process (Brown et al., 2000; Gavillon, 2007; Dickinson & Heal, 2009a, 2009b). This can be explained by the fact that, for solid state kinetics, unlike liquids and gases, it is possible to have a variation of the activation energies with conversion. This is due to the greater sensitivity of the solid phase reactions to pressure, temperature, crystal size, etc.

The isoconversional methods give values with real physical meaning for the activation energy; however, it is inappropriate to denote them as "model-free", since they only postpone the choice of a certain kinetic model until an estimate of the activation energy has been made, as outlined by Sewry and Brown (2002). Moreover, Capart et al. (2004) observed a qualitative agreement in the kinetic parameters obtained both from isoconversional and subsequent nonlinear regression methods. Among the authors interested in this field, Sergey Vyazovkin (Vyazovkin & Dollimore, 1996; Vyazovkin & Wight, 1997; Brown et al., 2000) and Nicolas Sbirrazzuoli (Sbirrazzuoli et al., 2009) made major valuable contributions. They outlined in their studies that isoconversional methods enable the acquisition of information on the controlling mechanisms for a global reaction. Furthermore, by applying these new methods, the same mathematical approach can be used in resolving the system of equations.

The isoconversional methods for the calculation of Arrhenius parameters are classified into two major types, in respect of the mathematical treatment applied to the TGA data. Thus, the approaches are either differential or integral, based on graphical methods and they require at least three experiments. Among the differential methods, Friedman method is the simplest and most frequently used. It is based on the rate equation's differential form (Capart et al., 2004; Aboulakas & Harfi, 2008):

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = \ln\left[Af(\alpha)\right] - \frac{E_\mathrm{a}}{RT} \tag{20}$$

where $\beta/(℃\ \mathrm{min^{-1}})$ is the heating rate.

As for the integral methods, the best-known is the Flynn–Wall–Ozawa (FWO) method which uses linear equations for calculation of E_a (Aboulakas & Harfi, 2008):

$$\ln\beta = \frac{\ln(AE_\mathrm{a})}{Rg(\alpha)} - 5.331 - 1.052\frac{E_\mathrm{a}}{RT} \tag{21}$$

where

$$g(\alpha) = \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{\mathrm{T_0}}^{T} \exp\left(-\frac{E_\mathrm{a}}{RT}\right)\mathrm{d}T = \\ = \frac{E_\mathrm{a}}{\beta R}p\left(\frac{E_\mathrm{a}}{RT}\right) \tag{22}$$

$f(\alpha)$ is the kinetic model of the process and $p(E_\mathrm{a}/RT)$ is Doyle's approximation for calculating the so-called "temperature integral" used in the isothermal model-fitting methods.

However, in this case, the solution of Eq. (21) uses several approximations which introduce some errors into the kinetic parameters values. In order to overcome this drawback, a non-linear isoconversional method was proposed by Vyazovkin and Dollimore (1996). This method is based on the minimum condition obtained from the integral form of the general Eq. (21):

$$\sum_{i}^{n}\sum_{j\neq i}^{n}\left[\frac{I\left(E_{\mathrm{a},\alpha};T_{\alpha,j}\right)\beta_{j}}{I\left(E_{\mathrm{a},\alpha};T_{\alpha,i}\right)\beta_{\mathrm{i}}}\right]=\min \tag{23}$$

where I is the identical matrix, n is the total number of experimental points and i, j are the numbers of the tested heating rates.

To avoid the use of an approximation for the temperature integral, the method proposed by Budrugeac and Segal (2003) can be used. This covers the case of solid–gas decomposition using isothermal experiments.

Other isoconversional methods cited in the literature are those proposed by Kissinger–Akahira–Sunose (Eq. (24)) (Aboulakas & Harfi, 2008) and Li–Tang (Eq. (25)) (Li & Tang, 1997, 1999):

$$\frac{\ln\beta}{T^{2}}=\frac{\ln\left(AR\right)}{E_{\mathrm{a}}\int\limits_{\alpha_{0}}^{\alpha}\frac{\mathrm{d}\alpha}{f\left(\alpha\right)}}-\frac{E_{\mathrm{a}}}{RT} \tag{24}$$

$$\int\limits_{\alpha_{0}}^{\alpha}\left(\ln\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)\mathrm{d}\alpha=-\frac{E_{\mathrm{a}}}{R}\int\limits_{\alpha_{0}}^{\alpha}\frac{1}{T}\mathrm{d}\alpha+G\left(\alpha,\alpha_{0}\right) \tag{25}$$

where:

$$G\left(\alpha,\alpha_{0}\right)=\ln A+\int\limits_{\alpha_{0}}^{\alpha}\ln\left(f\left(\alpha\right)\right)\mathrm{d}\alpha \tag{26}$$

and α_0 is the initial conversion considered.

Finally, this class of kinetic methods also includes the non-parameter kinetic (NPK) models (Sewry & Brown, 2002). These models assume that the reaction rate of a solid state reaction can be expressed as a product of two independent functions: one function depending on conversion and usually denoted as $g(\alpha)$ and the other depending on temperature and denoted as $f(T)$. It should be noted that, in this case, the form of $f(T)$ can be of a type other than the commonly used Arrhenius law type. This approximation is denoted as “single step” by Šimon (2005), and has the mathematical form expressed by the following equation

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=g\left(\alpha\right)f\left(T\right) \tag{27}$$

Several integral methods have already been standardised for the experimental use of TGA and DSC instruments (Capart et al., 2004). This is the case for the FWO (Flynn–Wall–Ozawa) method, the KAS (Kissinger–Akahira–Sunose) method and the different Vyazovkin methods. Other isoconversional expressions exist in the literature but are rarely used. Table 3 gives the literature kinetic parameters obtained with these models under different experimental conditions. It may be observed that, irrespective of the isoconversional kinetic model used, the heating rates (from slow to fast), the type and flow-rate value of the carrier gas, and the type of cellulose, the values are close to each other, especially for the activation energy. From this type of method, the mean value of the activation energy reviewed is very close to that obtained from the F1 model-fitting kinetic model, namely 194.3 kJ mol^{-1} from the isoconversional models vs 192.3 kJ mol^{-1} from the F1 model. This demonstrates that, among the model-fitting kinetic models, the F1 model is suited to accurately describing the kinetics of cellulose pyrolysis.

The isoconversional methods afford kinetic parameter values that can vary with conversion (Vyazovkin, 1996; Vyazovkin & Dollimore, 1996; Vyazovkin & Wight, 1997). In this case, E_a represents a temperature coefficient for the global reaction rate, showing the sensibility of this reaction rate to temperature. The other kinetic parameter, A, represents a scalar factor of the global reaction rate and characterises the reaction’s amplitude or intensity.

Discussion

Figs. 2a and 2b present the corresponding apparent activation energy and pre-exponential factor literature values previously listed in Tables 1–3. Only two sets (A and E) of the kinetic parameters listed in Table 3 are shown. The results are coherent but very scattered, confirming the influence of the heat transfer and experimental conditions (type of cellulose, mass of sample, heating rate, pyrolysis temperature, etc.) on the reaction kinetics. Regarding the values of the activation energy, Várhegyi et al. (1989) state that the highest values are the most reliable.

Fig. 2a shows that the highest values of the kinetic parameters from the first order kinetic model (F1) are obtained when using microcrystalline cellulose (MCC). Other types of cellulose also afford the same results. These were not identified in the references chosen but it is possible they also were MCC. The same order of magnitude for these parameters is obtained using isoconversional methods, as is also the case for MCC. However, these values are situated within the medium range of those obtained by using the F1 model. With regard to the isoconversional methods, it should be noted that the Friedman method gives higher values for the activation energy than the Capela–Ribeiro method.

Fig. 2b indicates that, in the case of the 3R model

Table 3. Published values for the kinetic parameters of isoconversional ("model-free") methods of cellulose pyrolysis in inert atmosphere

Reference	Isoconversional method	A	E_a	α	Cellulose type or source	Equipment	Heating rate	Temperature range	Carrier gas	Carrier gas flow	Sample mass
		min^{-1}	kJ mol^{-1}	%			°C min^{-1}	°C		mL min^{-1}	mg
Capart et al. (2004)	Kissinger	–	200.0	–	MCC – Whatman CC31	TGA 92[a]	1, 2, 3, 5, 10	RT to 700	N_2	1500	4–7
Capart et al. (2004)	Friedman	3.3×10^{16}	200.0	10–60	MCC – Whatman CC31	TGA 92[a]	1, 2, 3, 5, 10	RT to 700	N_2	1500	4–7
Kim and Eom (2006)	Tanaka	–	192.9	20–80	Refined pure cellulose powder	TGA ST-2960	5, 10, 20	RT to 650	N_2	50	7
Hu et al. (2007)	Ozawa	–	233.0	–	α-Cellulose – Fluka	EXSTAR600[b]	2.5, 5, 10	RT to 900	N_2	200	3–7
Cabrales and Abidi (2010)	Vyazovkin	–	164.0	5–85	MCC – Avicel PH105	Pyris1TGA[c]	4, 5, 8, 10, 16	150–600	N_2	20	2–3
Cabrales and Abidi (2010)	Vyazovkin	–	178.0	10–85	Cotton fibers (α-Cellulose)	Pyris1TGA[c]	4, 5, 8, 10, 16	150–600	N_2	20	2–3
Barud et al. (2011)	Capela–Ribeiro	6.3×10^{14}	182.3	–	MCC-Avicel	TA2960SDT[d]	5, 10, 20	40–450	N_2	100	~ 3
Tihay et al. (2011)	Friedman	–	207.6	20–55	Cellulose made from recycled paper	Setsys 16/18[a]	2, 5, 10, 20, 30	RT to 800	Ar	–	5
Sánchez-Jiménez et al. (2011)	Friedman	–	191.0	–	MCC - Aldrich	Q5000 IR[d]	1, 2, 5, 10	–	N_2	150	8–10

a) Setaram; *b*) Seiko Instruments; *c*) Perkin–Elmer; *d*) TA Instruments; RT = ambient temperature.

applied to a sample of α-cellulose, the activation energy required for the simultaneous formation of the three reaction products (char, tar, gases) is slightly higher than thatrequired for the formationof char: $\sim$ 200 kJ mol^{-1} vs $\sim$ 170 kJ mol^{-1}. When comparing the values of E_a for reaction Eq. (8) from two models using two different types of cellulose, Fig. 2b indicates that higher values are obtained for the α-cellulose (3R model, $\sim$ 200 kJ mol^{-1}) than for the filter paper (BSZ model, $\sim$ 150 kJ mol^{-1}).

It should also be noted that, for models BS, KB1, and DB, the values of the kinetic parameters are very close to each other, especially for reactions Eqs. (4), (10), and (12). Moreover, model AF exhibits slightly different values of these parameters when using different types of cellulose. Hence, reactions Eqs. (17) and (18) give values of activation energy in the range of 130–150 kJ mol^{-1} when using α-cellulose and of approximately 170 kJ mol^{-1} when using filter paper. The corresponding values of the pre-exponential factor range are: from 1.94×10^{11} min^{-1} up to 1.06×10^{13} min^{-1} for α-cellulose and approximately 5.75×10^{14} min^{-1} for filter paper. The reaction for the formation of intermediate from cellulose (reaction Eq. (4)) covers a wide range of values for the kinetic parameters. Thus, for the activation energy, these values are from approximately 130 kJ mol^{-1} up to 270 kJ mol^{-1}. The pre-exponential factor values are between 1.78×10^{8} min^{-1} and 7.58×10^{23} min^{-1}, respectively. The same behaviour can be observed for the reaction of tar formed from cellulose (reaction Eq. (2)): activation energy of 153–290 kJ mol^{-1} and pre-exponential factor of 1.58×10^{15}–5.62×10^{24} min^{-1}.

Regarding the reaction of intermediate-forming (reaction Eq. (4)) that remains controversial, different behaviours can be observed when using different kinetic models. Hence, from the MKB model, the value of activation energy for this reaction is lower than for the reaction of tar-forming from cellulose (reaction Eq. (2)). At the same time, this value is the highest when using BS, DB, and DKM models. It is superior to the E_a of the intermediate decomposition to the pyrolysis products. This renders this reaction very slow in comparison with the others. Consequently, the intermediate-forming could be ignored in the kinetic models for this process.

Conclusions

This paper presents a short review of the main kinetic models published for cellulose pyrolysis. All of these models are to varying extents empirical, hence their degree of validity is generally limited to the particular conditions used in their development (quality of cellulose, heating rate, nature, flow-rate of carrier gas, etc.). They are classified into two major types: "model-fitting" and "model-free" (isoconver-

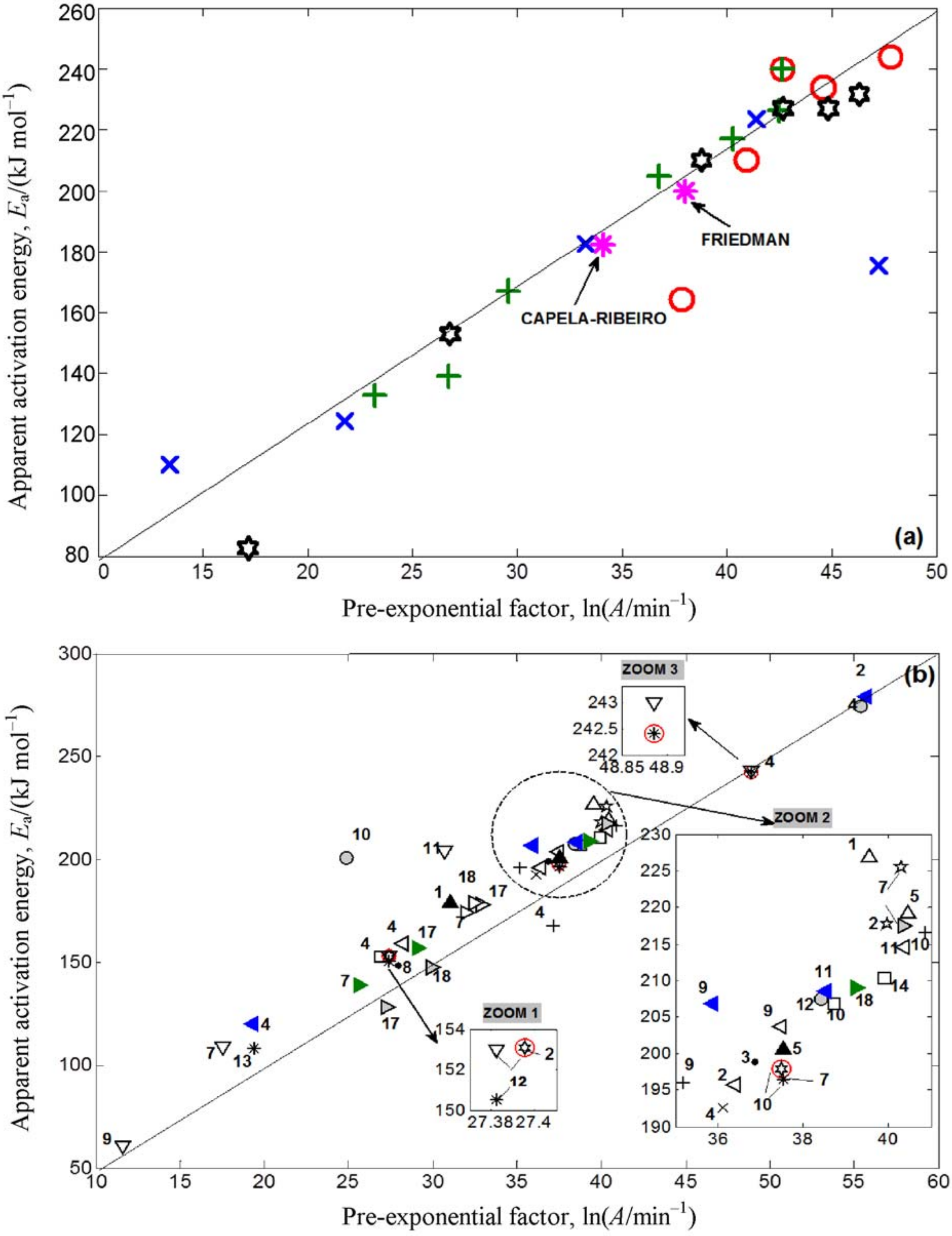

Fig. 2. Compensation plots of several Arrhenius parameters from the literature (E_a vs ln$A$) for cellulose pyrolysis. F1 (MCC (○), α-cellulose (×), filter paper (+), cellulose (✡)) and isoconversional (∗) kinetic models (Tables 1 and 3) (a) and semi-global kinetic models KB1 (1975 (✡), 1995 (☆)), BR (1998 (⊡)), BS (1979 (○), 1995 filter paper (●)), DKM (1987 (▽)), 3R (α-cellulose: 1988 (▲) 1995 (△)), MKB (α-cellulose: 1988 (◁), 1995 (◀)), AF (1989: filter paper (▷), α-cellulose (▶), 1995 filter paper (▷)), DB (1994 (∗)), KB (1997 (+)), BSZ (2001 filter paper (●)), F (2008 (×)) models (Table 2) (b).

sional) methods. The first type uses a pre-defined mathematical model for the process and fits the experimental data on it while the second postpones the choice of a model by first finding a variation in the activation energy with the degree of conversion for the process studied.

The kinetic models most frequently used for cellulose pyrolysis have been the F1 and BS (Broido–Shafizadeh) models. The latter currently acts as a reference for this process. When comparing the kinetic parameters values obtained from all these studies in the literature, a significant scattering could be observed but, nevertheless, a coherence. The differences are explained by the dissimilar experimental conditions and the lack of physical meaning of rate expressions and parameters, as observed by Galwey (2004). When using the F1 model, the highest values of the kinetic parameters were obtained in the case of microcrystalline cellulose (MCC).

From a comparison of several values of these parameters, when using semi-global kinetic models, it was concluded that the formation of an intermediate could be ignored due to the very high values obtained for the rate of this reaction.

The author suggests that the F1 kinetic model could be used for the design of a pyrolysis industrial plant, as a first approximation and for a general view of the process. For more accurate calculus, some isoconversional method must be used.

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References

Aboulkas, A., & El Harfi, K. (2008). Study of the kinetics and mechanisms of thermal decomposition of Moroccan Tarfaya oil shale and its kerogen. *Oil Shale*, *25*, 426–443. DOI: 10.3176/oil.2008.4.04.

Alves, S. S., & Figueiredo, J. L. (1989). Kinetics of cellulose pyrolysis modelled by three consecutive first-order reactions. *Journal of Analytical and Applied Pyrolysis*, *17*, 37–46. DOI: 10.1016/0165-2370(89)85004-1.

AGEE-Stat (2011). *Renewable energy sources 2010.* Bonn, Germany: Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.

Agrawal, R. K. (1988). Kinetics of reactions involved in pyrolysis of cellulose. II. The modified Kilzer-Broido model. *The Canadian Journal of Chemical Engineering*, *66*, 413–418. DOI: 10.1002/cjce.5450660310

Banyasz, J. L., Li, S., Lyons-Hart, J. L., & Shafer, K. H. (2001). Cellulose pyrolysis: the kinetics of hydroxyacetaldehyde evolution. *Journal of Analytical and Applied Pyrolysis*, *57*, 223–248. DOI: 10.1016/s0165-2370(00)00135-2.

Barud, H. S., Ribeiro, C. A., Capela, J. M. V., Crespi, M. S., Ribeiro, S. J. L., & Messadeq, Y. (2011). Kinetic parameters for thermal decomposition of microcrystalline, vegetal, and bacterial cellulose. *Journal of Thermal Analysis and Calorimetry*, *105*, 421–426. DOI: 10.1007/s10973-010-1118-9.

Blažek, J. (2005). *Study of the reaction kinetics of the thermal degradation of polymer.* Ph. D. thesis, Institut National Polytechnique de Toulouse, Toulouse, France.

Broido, A., Javier-Son, A. C., Ouano, A. C., Barrell, E. M., II (1973). Molecular weight decrease in the early pyrolysis of crystalline and amorphous cellulose. *Journal of Applied Polymer Science*, *17*, 3627–3635. DOI: 10.1002/app.1973.070171207.

Broido, A., & Nelson, M. A. (1975). Char yield on pyrolysis of cellulose. *Combustion and Flame*, *24*, 263–268. DOI: 10.1016/0010-2180(75)90156-x.

Broido, A. (1976). Kinetics of solid-phase cellulose pyrolysis. In F. Shafizadeh, K. V. Sarkanen, & D. A. Tillman (Eds.), *Thermal uses and properties of carbohydrates and lignins* (pp. 19–36). New York, NY, USA: Academic Press. DOI: 10.1016/b978-0-12-637750-7.50006-6.

Brown, M. E., Maciejewski, M., Vyazovkin, S., Nomen, R., Sempere, J., Burnham, A., Opfermann, J., Strey, R., Anderson, H. L., Kemmler, A., Keuleers, R., Janssens, J., Desseyn, H. O., Li, C. R., Tang, T. B., Roduit, B., Malek, J., & Mitsuhashi, T. (2000). Computational aspects of kinetic analysis. Part A: The ICTAC kinetics project-data, methods and results. *Thermochimica Acta*, *355*, 125–143. DOI: 10.1016/s0040-6031(00)00443-3.

Budrugeac, P., & Segal, E. (2003). Prediction of the isothermal behavior of solid-gas systems from non-isothermal data. *Journal of Thermal Analysis and Calorimetry*, *72*, 831–837. DOI: 10.1023/a:1025014114527.

Cabrales, L., & Abidi, N. (2010). On the thermal degradation of cellulose in cotton fibers. *Journal of Thermal Analysis and Calorimetry*, *102*, 485–491. DOI: 10.1007/s10973-010-0911-9.

Capart, R., Khezami, L., & Burnham, A. K. (2004). Assessment of various kinetic models for the pyrolysis of a microgranular cellulose. *Thermochimica Acta*, *417*, 79–89. DOI: 10.1016/j.tca.2004.01.029.

Chen, W. H., & Kuo, P. C. (2011). Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. *Energy*, *36*, 6451–6460. DOI: 10.1016/j.energy.2011.09.022.

Conesa, J. A., Caballero, J. A., Marcilla, A., & Font, R. (1995). Analysis of different kinetic models in the dynamic pyrolysis of cellulose. *Thermochimica Acta*, *254*, 175–192. DOI: 10.1016/0040-6031(94)02102-t.

Di Blasi, C. (1993). Modeling and simulation of combustion processes of charring and non-charring solid fuels. *Progress in Energy and Combustion Science*, *19*, 71–104. DOI: 10.1016/0360-1285(93)90022-7.

Di Blasi, C. (1996). Heat transfer mechanisms and multistep kinetics in the ablative pyrolysis of cellulose. *Chemical Engineering Science*, *51*, 2211–2220. DOI: 10.1016/0009-2509(96)00078-4.

Di Blasi, C. (1998). Comparison of semi-global mechanisms for primary pyrolysis of lignocellulosic fuels. *Journal of Analytical and Applied Pyrolysis*, *47*, 43–64. DOI: 10.1016/s0165-2370(98)00079-5.

Dickinson, C. F., & Heal, G. R. (2009a). A review of the ICTAC Kinetics Project, 2000. Part 1. Isothermal results. *Thermochimica Acta*, *494*, 1–14. DOI: 10.1016/j.tca.2009.05.003.

Dickinson, C. F., & Heal, G. R. (2009b). A review of the ICTAC kinetics project, 2000. Part 2. Non-isothermal results. *Thermochimica Acta*, *494*, 15–25. DOI: 10.1016/j.tca.2009.05.009.

Diebold, J. P. (1994). A unified, global model for the pyrolysis of cellulose. *Biomass and Bioenergy*, *7*, 75–85. DOI: 10.1016/0961-9534(94)00039-v.

Evans, R. J., & Milne, T. A. (1987). Molecular characterization of the pyrolysis of biomass. 1. Fundamentals. *Energy & Fuels*, *1*, 123–137. DOI: 10.1021/ef00002a001.

Fisher, T., Hajaligol, M., Waymack, B., & Kellogg, D. (2002). Pyrolysis behavior and kinetics of biomass derived materials. *Journal of Analytical and Applied Pyrolysis*, *62*, 331–349. DOI: 10.1016/s0165-2370(01)00129-2.

Font, R., & García, A. N. (1995). Application of the transition state theory to the pyrolysis of biomass and tars. *Journal of Analytical and Applied Pyrolysis*, *35*, 249–258. DOI: 10.1016/0165-2370(95)00916-8.

Galwey, A. K. (2004). Is the science of thermal analysis kinetics based on solid foundations? A literature appraisal. *Thermochimica Acta*, *413*, 139–183. DOI: 10.1016/j.tca.2003.10.013.

Garcia-Perez, M. (2008). *The formation of polyaromatic hydrocarbons and dioxins during pyrolysis: A review of the literature with descriptions of biomass composition, fast pyrolysis technologies and thermochemical reactions*. Pullman, WA, USA: Washington State University. (WSUEEP08-010)

Gavillon, R. (2007). *Préparation et caractérisation des matériaux cellulosiques ultra poreux*. Ph. D. thesis, École des Mines de Paris, Paris, France. (in French)

Grønli, M., Antal, M. J., Jr., & Várhegyi, G. (1999). A round-robin study of cellulose pyrolysis kinetics by thermogravimetry. *Industrial & Engineering Chemistry Research*, *38*, 2238–2244. DOI: 10.1021/ie980601n.

Hopkins, M. W., DeJenga, C., & Antal, M. J., Jr. (1984). The flash pyrolysis of cellulosic materials using concentrated visible light. *Solar Energy*, *32*, 547–551. DOI: 10.1016/0038-092x(84)90269-x.

Hu, S., Jess, A., & Xu, M. H. (2007). Kinetic study of Chinese biomass slow pyrolysis: Comparison of different kinetic models. *Fuel*, *86*, 2778–2788. DOI: 10.1016/j.fuel.2007.02.031.

Huang, Y. F., Kuan, W. H., Chiueh, P. T., & Lo, S. L. (2011). A sequential method to analyze the kinetics of biomass pyrolysis. *Bioresource Technology*, *102*, 9241–9246. DOI: 10.1016/j.biortech.2011.07.015.

Kim, S. D., & Eom, Y. J. (2006). Estimation of kinetic triplet of cellulose pyrolysis reaction from isothermal kinetic results. *Korean Journal of Chemical Engineering*, *23*(3), 409–414. DOI: 10.1007/bf02706742.

Kilzer, F. J., & Broido, A. (1965). Speculations on the nature of cellulose pyrolysis. *Pyrodynamics*, *2*, 151–163.

Lédé, J. (2012). Cellulose pyrolysis kinetics: An historical review on the existence and role of intermediate active cellulose. *Journal of Analytical and Applied Pyrolysis*, *94*, 17–32. DOI: 10.1016/j.jaap.2011.12.019.

Lewellen, P. C., Peters, W. A., & Howard, J. B. (1977). Cellulose pyrolysis kinetics and char formation mechanism. *Symposium (International) on Combustion*, *16*, 1471–1480. DOI: 10.1016/s0082-0784(77)80429-3.

Li, C. R., & Tang, T. B. (1997). Dynamic thermal analysis of solid-state reactions. The ultimate method for data analysis? *Journal of Thermal Analysis*, *49*, 1243–1248. DOI: 10.1007/bf01983680.

Li, C. R., & Tang, T. B. (1999). Isoconversional method for kinetic analysis of solid-state reactions from dynamics thermoanalytical data. *Journal of Materials Science*, *34*, 3467–3470. DOI: 10.1023/a:1004605820783.

Liao, Y. F., Wang, S. R., & Ma, X. Q. (2004). Study of reaction mechanisms in cellulose pyrolysis. *Preprints of Papers-American Chemical Society, Division of Fuel Chemistry*, *49*, 407–411.

Liu, Q., Wang, S. R., Wang, K. G., Guo, X. J., Luo, Z. Y., & Cen, K. F. (2008). Mechanism of formation and consequent evolution of active cellulose during cellulose pyrolysis. *Acta Physico-Chimica Sinica*, *24*, 1957–1963. DOI: 10.1016/s1872-1508(08)60078-9.

Mamleev, V., Bourbigot, S., & Yvon, J. (2007). Kinetic analysis of the thermal decomposition of cellulose: The change of the rate limitation. *Journal of Analytical and Applied Pyrolysis*, *80*, 141–150. DOI: 10.1016/j.jaap.2007.01.012.

Mamleev, V., Bourbigot, S., Le Bras, M., & Yvon, J. (2009). The facts and hypotheses relating to phenomenological model of cellulose pyrolysis: Interdependence of the steps. *Journal of Analytical and Applied Pyrolysis*, *84*, 1–17. DOI: 10.1016/j.jaap.2008.10.014.

Marra, F. (2009). Numerical analysis for kinetics and yield of wood biomass pyrolysis. In N. Mastorakis, & J. Sakellaris (Eds.), *Advances in numerical methods* (chapter 11, pp. 127–136). Heidelberg, Germany: Springer. DOI: 10.1007/978-0-387-76483-211.

Miller, R. S., & Bellan, J. (1997). A generalized biomass pyrolysis model based on superimposed cellulose, hemicellulose and lignin kinetics. *Combustion Science and Technology*, *126*, 97–137. DOI: 10.1080/00102209708935670.

Ranzi, E., Cuoci, A., Faravelli, T., Frassoldati, A., Migliavacca, G., Pierucci, S., & Sommariva, S. (2008). Chemical kinetics of biomass pyrolysis. *Energy & Fuels*, *22*, 4292–4300. DOI: 10.1021/ef800551t.

Reed, T. B., & Cowdery, C. D. (1987). Heat flux requirements for fast pyrolysis and a new method for generating biomass vapor. In *193rd National Meeting of the American Chemical Society*, April 5–10, 1987. Denver, CO, USA: American Chemical Society Division of Petroleum Chemistry.

Sánchez-Jiménez, P. E., Pérez-Maqueda, L. A., Perejón, A., Pascual-Cosp, J., Benítez-Guerrero, M., & Criado, J. M. (2011). An improved model for the kinetic description of the thermal degradation of cellulose. *Cellulose*, *18*, 1487–1498. DOI: 10.1007/s10570-011-9602-3.

Sbirrazzuoli, N., Vincent, L., Mija, A., & Guigo, N. (2009). Integral, differential and advanced isoconversional methods. Complex mechanisms and isothermal predicted conversion-time curves. *Chemometrics and Intelligent Laboratory Systems*, *96*, 219–226. DOI: 10.1016/j.chemolab.2009.02.002.

Scott, D. S., Piskorz, J., & Radlein, D. (1989). Thermal conversion of biomass to liquids by the Waterloo fast pyrolysis process. In E. Mattucci, G. Grassi, & W. Palz (Eds.), *Proceedings of Pyrolysis as a Basic Technology for Large Agro-Energy Projects*, October 15–16, 1987 (pp. 115–124). Brussels, Belgium: Office for Official Publications of the European Communities.

Sewry, J. D., & Brown, M. E. (2002). "Model-free" kinetic analysis? *Thermochimica Acta*, *390*, 217–225. DOI: 10.1016/s0040-6031(02)00083-7.

Shafizadeh, F. (1968). Pyrolysis and combustion of cellulosic materials. *Advances in Carbohydrate Chemistry*, *23*, 419–474. DOI: 10.1016/s0096-5332(08)60173-3.

Shafizadeh, F., & Bradbury, A. G. W. (1979). Thermal degradation of cellulose in air and nitrogen at low temperatures. *Journal of Applied Polymer Science*, *23*, 1431–1442. DOI: 10.1002/app.1979.070230513.

Shafizadeh, F. (1982). Introduction to pyrolysis of biomass. *Journal of Analytical and Applied Pyrolysis*, *3*, 283–305. DOI: 10.1016/0165-2370(82)80017-x.

Šimon, P. (2005). Considerations on the single-step kinetics approximation. *Journal of Thermal Analysis and Calorimetry*, *82*, 651–657. DOI: 10.1007/s10973-005-0945-6.

Sonobe, T., & Worasuwannarak, N. (2008). Kinetic analyses of biomass pyrolysis using the distributed activation energy model. *Fuel*, *87*, 414–421. DOI: 10.1016/j.fuel.2007.05.004.

Stamm, A. J. (1956). Thermal degradation of wood and cellulose. *Industrial & Engineering Chemistry*, *48*, 413–417. DOI: 10.1021/ie51398a022.

Tihay, V., Boulnois, C., & Gillard, P. (2011). Influence of oxygen concentration on the kinetics of cellulose wadding degradation. *Thermochimica Acta*, *525*, 16–24. DOI: 10.1016/j.tca.2011.07.016.

Várhegyi, G., Antal, M. J., Jr., Szekely, T., & Szabó, P. (1989). Kinetics of the thermal decomposition of cellulose, hemicellulose, and sugarcane bagasse. *Energy & Fuels*, *3*, 329–335. DOI: 10.1021/ef00015a012.

Várhegyi, G., Jakab, E., & Antal, M. J., Jr. (1994). Is the Broido-Shafizadeh model for cellulose pyrolysis true? *Energy & Fuel*, *8*, 1345–1352. DOI: 10.1021/ef00048a025.

Várhegyi, G., Antal, M. J., Jr., Jakab, E., & Szabó, P. (1997). Kinetic modeling of biomass pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *42*, 73–87. DOI: 10.1016/s0165-2370(96)00971-0.

Völker, S., & Rieckmann, Th. (2002). Thermogravimetric investigation of cellulose pyrolysis – impact of initial and final mass on kinetic results. *Journal of Analytical and Applied Pyrolysis*, *62*, 165–177. DOI: 10.1016/s0165-2370(01)00113-9.

Vyazovkin, S. (1996). A unified approach to kinetic processing of nonisothermal data. *International Journal of Chemical Kinetics*, *28*(2), 95–101. DOI: 10.1002/(SICI)1097-4601(1996)28:2<95::AID-KIN4>3.0.CO;2-G.

Vyazovkin, S., & Dollimore, D. (1996). Linear and nonlinear procedures in isoconversional computations of the activation energy of nonisothermal reactions in solids. *Journal of Chemical Information and Modeling*, *36*, 42–45. DOI: 10.1021/ci950062m.

Vyazovkin, S., & Wight, C. A. (1997). Kinetics in solids. *Annual Review of Physical Chemistry*, *48*, 125–149. DOI: 10.1146/annurev.physchem.48.1.125.

White, J. E., Catallo, W. J., & Legendre, B. L. (2011). Biomass pyrolysis kinetics: A comparative critical review with relevant agricultural case studies. *Journal of Analytical and Applied Pyrolysis*, *91*, 1–33. DOI: 10.1016/j.jaap.2011.01.004.

Zhu, G. Y., Zhu, X., Xiao, Z. B., & Yi, F. P. (2012). Study of cellulose pyrolysis using an in situ visualization technique and thermogravimetric analyzer. *Journal of Analytical and Applied Pyrolysis*, *94*, 126–130. DOI: 10.1016/j.jaap.2011.11.016.